INTRODUCTION
to the Computational Laboratory

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the London Centre for Theory and Simulation of Materials

19 January 2009 – 23 February 2009

Outline

TIMETABLE and DEADLINE → GROUP A

- The Electronic Structure of Molecules, Polymers, Surfaces and Solids

	Mon	Tue	Thur	Fri
2:00-5:00	23/02/09	24/02/09	26/02/09	27/02/09

DEADLINE:

when? **13:00am on Wed the 3rd of March**
where? ROOM 442 to Ms Lisa Benbow

- Statistical Mechanics: The Thermal Expansion of MgO

	Mon	Tue	Thur	Fri
2:00-5:00	08/03/09	09/03/09	11/03/09	12/03/09

DEADLINE:

when? **13:00pm on Wed the 15th of March**
where? ROOM 442 to Ms Lisa Benbow

TIMETABLE and DEADLINE → GROUP B

- The Electronic Structure of Molecules, Polymers, Surfaces and Solids

	Mon	Tue	Thur	Fri
2:00-5:00	19/01/09	20/01/09	22/01/09	23/01/09

DEADLINE:

when? **13:00am on Wed the 28th of January**
where? ROOM 442 to Ms Lisa Benbow

- Statistical Mechanics: The Thermal Expansion of MgO

	Mon	Tue	Thur	Fri
2:00-5:00	02/02/09	03/02/09	05/02/09	06/02/09

DEADLINE:

when? **13:00pm on Wed the 11th of February**
where? ROOM 442 to Ms Lisa Benbow

AIM: The Electronic Structure of Molecules, Polymers, Surfaces and Solids

- to show that a solid can be considered as an infinite molecule
- to understand how the **energy level diagram** of a molecule (a finite system) becomes a **band structure** for a periodic system, like a polymer/chain, a slab/layer and a crystal.
- to connect the band structure of a system with its density of state (DOS)
- to analyse the band structure of a generic periodic system under investigation and to predict its electronic properties, depending on the band structure.

SYSTEMS

1. FINITE SYSTEMS:
   - the H atom $\rightarrow$ THE STARTING POINT
   - the H_2 molecule
   - the hypothetical **linear and cyclic** H_n clusters, with $n = 3, 4, ..., 100$
2. INFINITE SYSTEMS:
   - Polymer/Chain: the 1D periodic system
   - Slab/Layer: the 2D periodic system
   - Crystal: the 3D periodic system

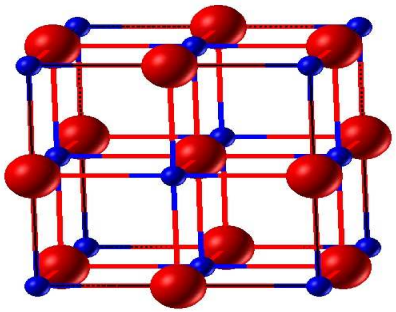
AIM:
The Thermal Expansion of MgO

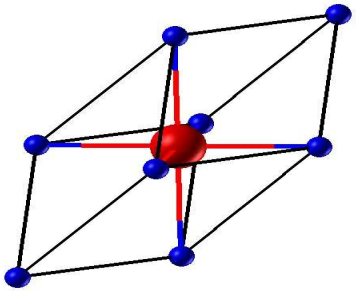
- to predict how the material expands when heated;
- to calculate the thermal expansion coefficient:
  $\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$
- **QUASI-HARMONIC APPROXIMATION** (LD)
  to compute vibrational energy levels of MgO;
  to understand the **phonon dispersion** of a material and the vibrational density of state;
- **MOLECULAR DYNAMICS** (MD)
  to simulate the vibrations as random motions of atoms inside a cell;
- to compare QUASI-HARMONIC APPROXIMATION with MOLECULAR DYNAMICS results.

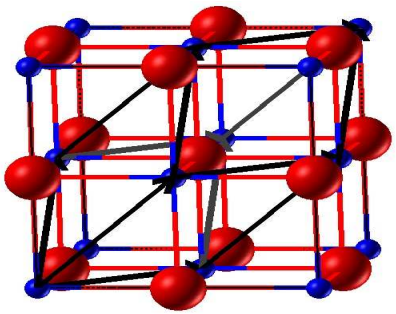
SYSTEMS: MgO crystal (fcc)

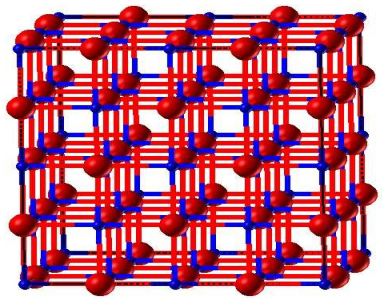
IDEAL, NON DEFECTIVE, PERIODIC SYSTEM IN 3D

- CONVENTIONAL CELL
  $\mathbf{a}_c$=$\mathbf{b}_c$=$\mathbf{c}_c$; α_c, β_c, γ_c
  N_c: number of atoms
  V_c: volume
- PRIMITIVE CELL
  $\mathbf{a}_p$=$\mathbf{b}_p$=$\mathbf{c}_p$; α_p, β_p, γ_p
  N_c: number of atoms
  V_p: volume
- SUPERCELL
  $\mathbf{a}_s$=$\mathbf{b}_s$=$\mathbf{c}_s$= 2 $\times$ $\mathbf{a}_c$
  α_s, β_s, γ_s
  N_s: number of atoms
  V_s: volume









HOW?

COMPUTATIONAL EXPERIMENT / SIMULATION

- program
- input

Environment:
the choice of the Operating System $\longrightarrow$ **linux**

Interface:
DLV = package for the visualisation of materials structures and properties.

SIMULATION TYPES

- CLASSICAL SIMULATION
  Newton law
- QUANTUM-MECHANICAL SIMULATION
  Schroedinger equation

Systems under investigation

Properties

Accuracy

Computational time

Resources

QUANTUM-MECHANICAL SIMULATION

SCHROEDINGER EQUATION

Nonrelativistic time-dependent

$$H|\Phi>= i\hbar\frac{\partial|\Phi>}{\partial t}$$

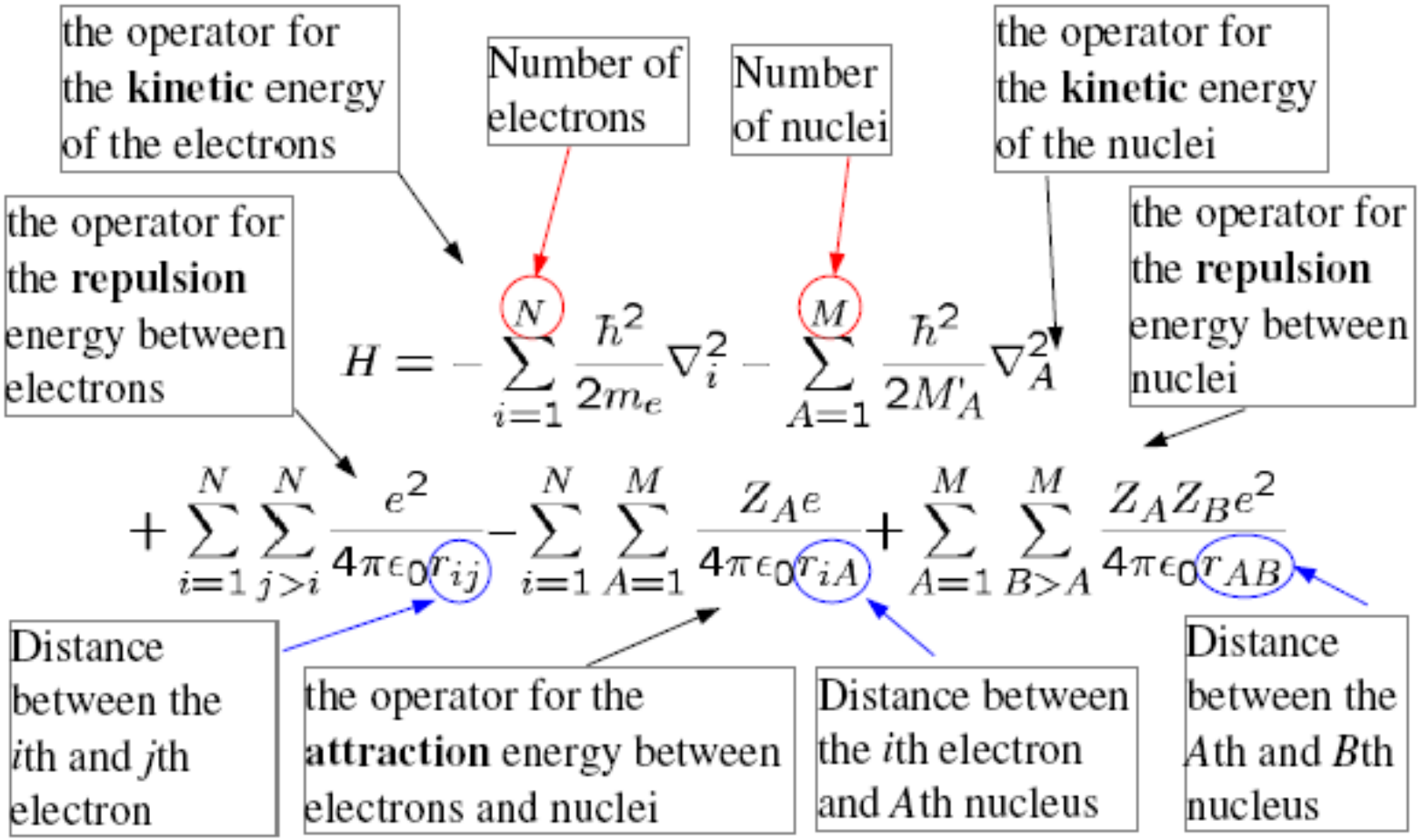
evolution of a system with time

Nonrelativistic time-independent

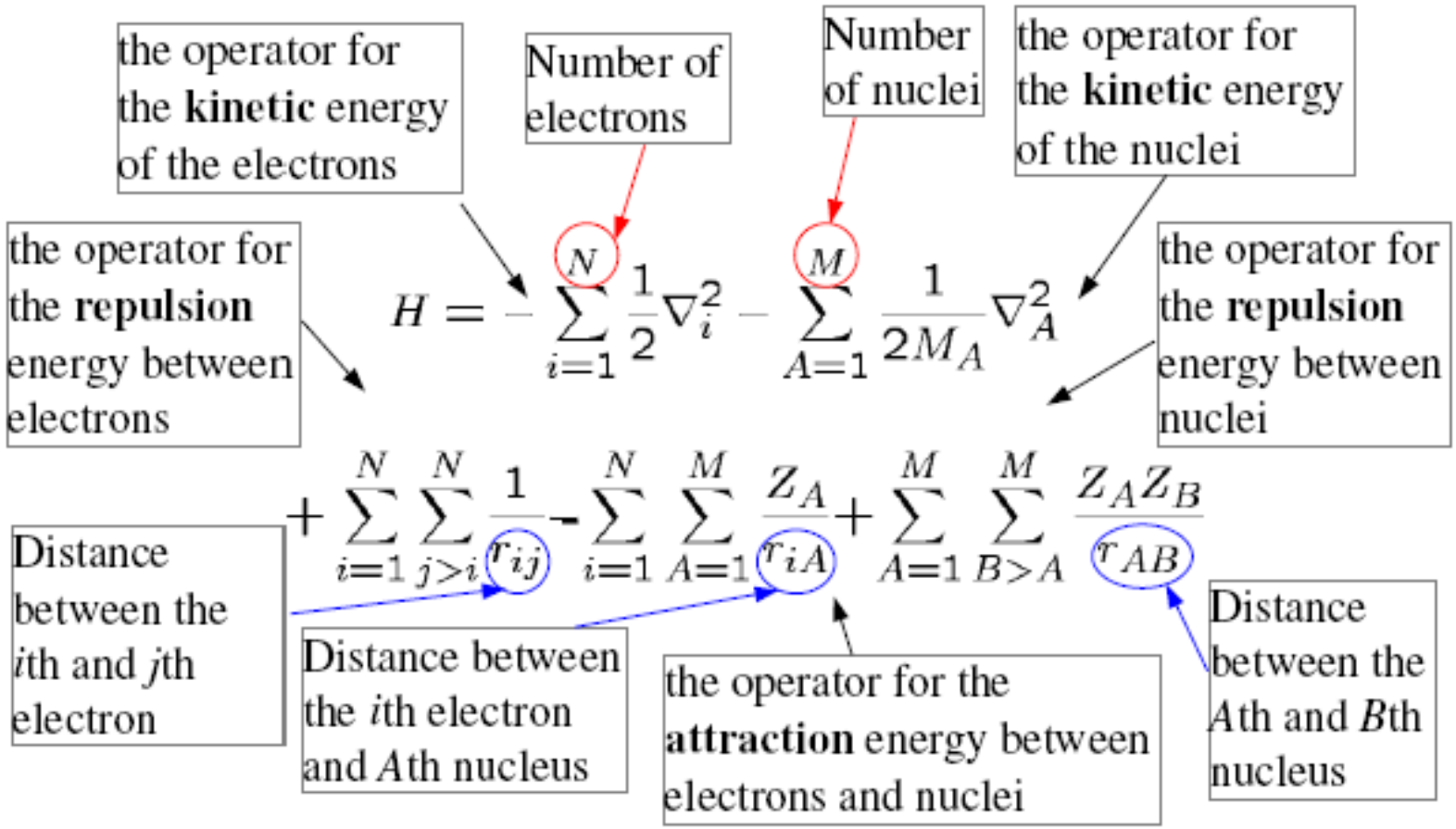
$$H|\Phi>= E|\Phi>$$

H is the Hamiltonian operator for a system of nuclei and electrons

HAMILTONIAN OPERATOR FOR A SYSTEM OF NUCLEI AND ELECTRONS



HAMILTONIAN OPERATOR FOR A SYSTEM OF NUCLEI AND ELECTRONS IN ATOMIC UNITS



SCHROEDINGER EQUATION: SOLUTIONS

- Hydrogen atom and hydrogenic atoms
  (H, He^{+}, Li^{2+}, ..., U^{91+})
  EXACT SOLUTION wavefunction
  coordinates of a single electron
- He, Hydrogen molecule, H_2^+
  APPROXIMATED SOLUTION wavefunction
  coordinates of all electrons manybody system

BORN-OPPENHEIMER APPROXIMATION

Nuclei, being so much heavier than electrons, move relatively slowly and may be treated as stationary while the electrons move in their field.

$$H_{elec} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}}$$

$$H_{elec}\Phi_{elec} = E_{elec}\Phi_{elec}$$

$$\Phi_{elec} = \Phi_{elec}(\{\mathbf{r}_i\};\{\mathbf{r}_A\})$$

explicit dependence on the electron coordinates: $\mathbf{r}_i$
parametric dependence on the nuclear coordinates: $\mathbf{r}_A$

$$E_{tot} = E_{elec} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{r_{AB}}$$

HARTREE-FOCK METHOD

The essence of HF approximation is to replace the complicated many electron problem by a one electron problem.

Fock operator

$$\hat{f}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + v^{HF}(i)$$

$v^{HF}(i)$ the average potential experienced by the ith electron due to the presence of the other electrons

$$f(i)\psi_{i,\alpha}(\mathbf{r_1}) = \epsilon_i\psi_{i,\alpha}(\mathbf{r_1})$$

where $\psi_i(\mathbf{r_1})$ ia a molecular/cristalline orbital
ϵ_i is the molecular/cristalline orbital energy

WAVEFUNCTION

$$\Phi(\mathbf{x_1}, ..., \mathbf{x_i}, ..., \mathbf{x_j}, ..., \mathbf{x_N})$$

N is the number of electrons

To complete describe an electron is necessary to specify its spin.

$$\mathbf{x} = \{\mathbf{r}, \mathbf{x}\}$$

where $x = \alpha$ or β

FROM HARTREE PRODUCT TO SLATER DETERMINANT

HARTREE PRODUCT

$$\psi_{i,\alpha}(\mathbf{r_1})\psi_{i,\beta}(\mathbf{r_2})\psi_{j,\alpha}(\mathbf{r_3})\psi_{j,\beta}(\mathbf{r_4})...\psi_{k,\alpha}(\mathbf{r_{N-1}})\psi_{k,\beta}(\mathbf{r_N})$$

Pauli principle:
No more than two electrons may occupy any given orbital and, if two do occupy one orbital, then their spin must be paired.

SLATER DETERMINANT

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i,\alpha}(\mathbf{r_1}) & \psi_{i,\beta}(\mathbf{r_1}) & \dots & \psi_{k,\beta}(\mathbf{r_1}) \\ \psi_{i,\alpha}(\mathbf{r_2}) & \psi_{i,\beta}(\mathbf{r_2}) & \dots & \psi_{k,\beta}(\mathbf{r_2}) \\ \dots & \dots & \dots & \dots \\ \psi_{i,\alpha}(\mathbf{r_N}) & \psi_{i,\beta}(\mathbf{r_N}) & \dots & \psi_{k,\beta}(\mathbf{r_N}) \end{vmatrix}$$

VARIATIONAL PRINCIPLE

According to the variation principle for the ground state $|\Phi_0>$, the energy of an approximate wave function $|\tilde{\Phi}>$ is always higher.

$$H|\Phi_0> = E_0|\Phi_0>$$

$$E_0 = \frac{\int \Phi_0^* H \Phi_0 d\tau}{\int \Phi_0^* \Phi_0 d\tau}$$

$$E_{\tilde{\Phi}} = \frac{\int \tilde{\Phi}^* H \tilde{\Phi} d\tau}{\int \tilde{\Phi}^* \tilde{\Phi} d\tau}$$

$$E_{\tilde{\Phi}} \geq E_0$$

Thus one measure of the quality of a wave function is its energy:
The lower the energy, the better the wave function.

SELF CONSISTENT FIELD

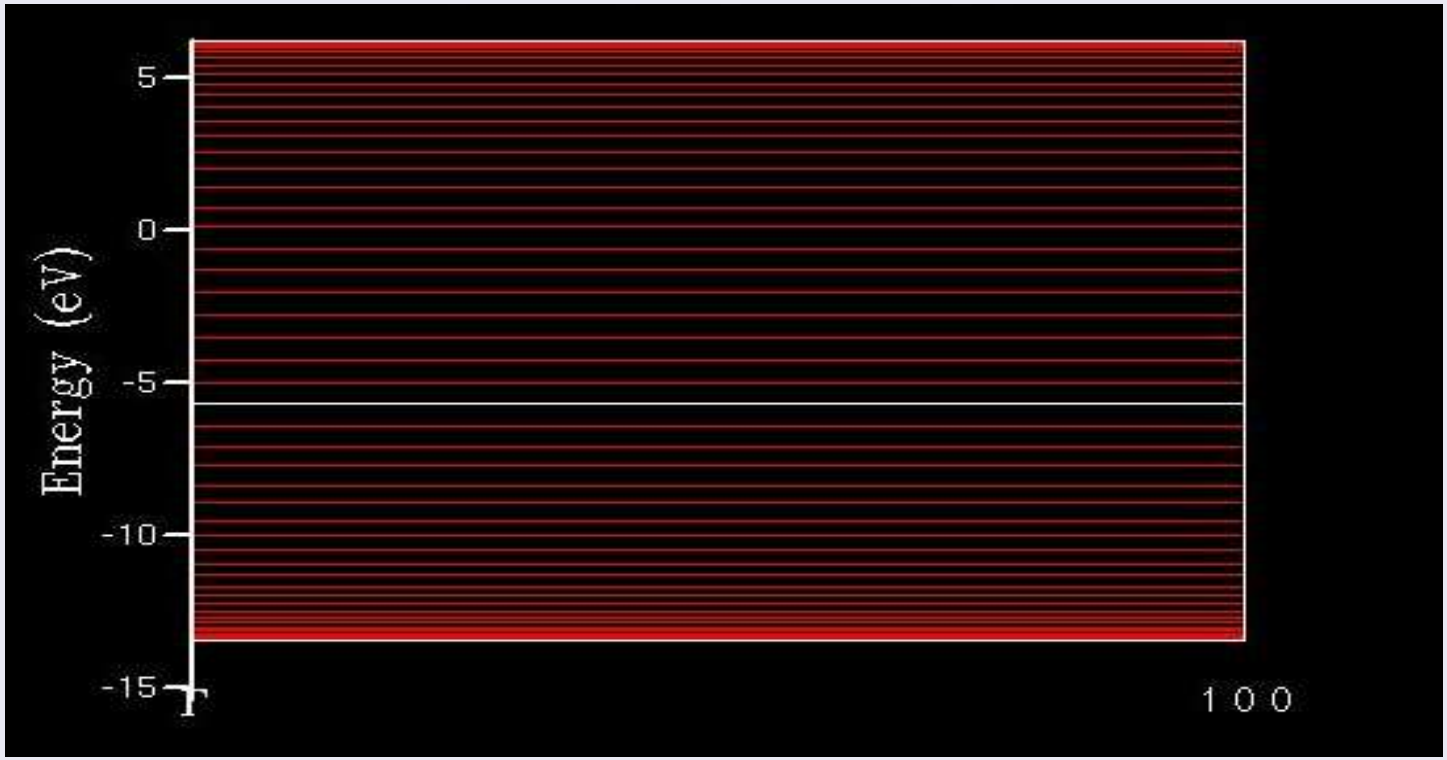
The HF potential $v^{HF}(i)$ depends on the other electrons.
The HF equation, $f(i)\psi_{i,\alpha}(\mathbf{r_1}) = \epsilon_i \psi_{i,\alpha}(\mathbf{r_1})$ is NONLINEAR and must be solve iteratively.
The procedure for solving the HF equation is called self-consistent-field (SCF) method

1. to make an initial guess of the spin orbitals ($\psi(\mathbf{r})\alpha$ or $\psi(\mathbf{r})\beta$: the wave function of an electron describing both its spatial distribution and its spin);
2. to calculate the average potential $v^{HF}(i)$;
3. to solve the HF equation for a new set of spin orbitals
4. to repeat until there are no change in the potential;

RESULTS: FINITE SYSTEMS

Energy level diagram for H_{100}

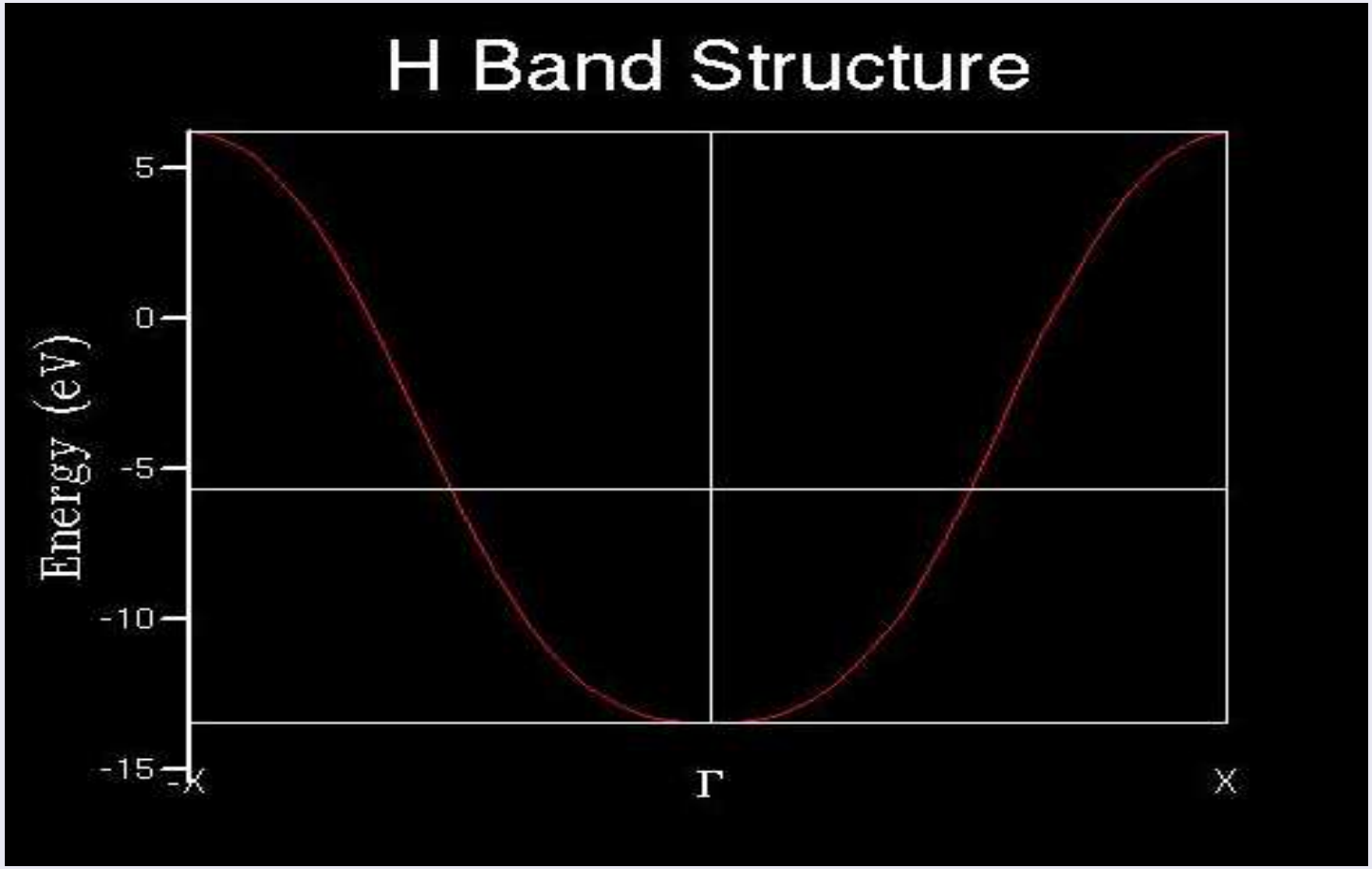
Number of molecular orbitals = Number of atomic orbitals



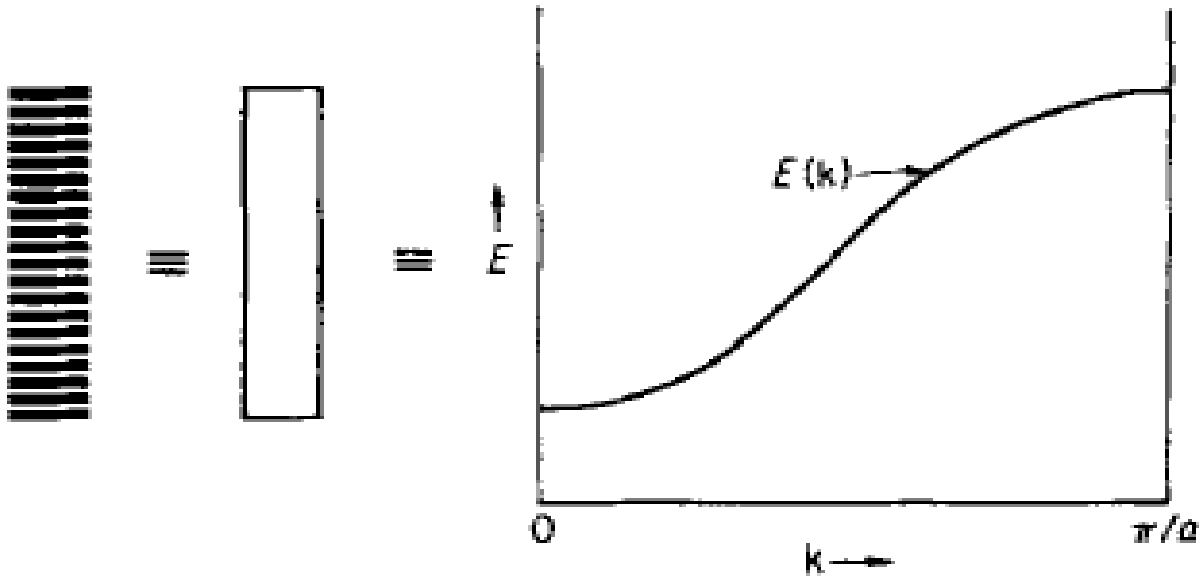
RESULTS: INFINITE SYSTEMS (PERIODIC)

Band structure

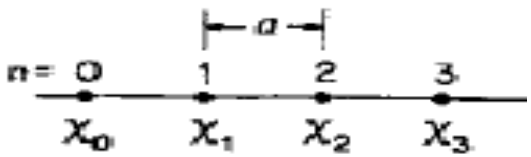
Number of bands = Number of atomic orbitals



BLOCK FUNCTION



Block function



$$\psi_k = \sum_n e^{ikna} \, x_n$$

$k = 0 \qquad \psi_0 = \sum_n e^0 \, x_n = \sum_n x_n = x_0 + x_1 + x_2 + x_3 + \cdots$

$k = \frac{\pi}{a} \qquad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n} \, x_n = \sum_n (-1)^n \, x_n = x_0 - x_1 + x_2 - x_3 + \cdots$

BLOCH'S THEOREM IN 1D

1D periodic potential

$$V(x+na) = V(x)$$

1D periodic electronic density

$$\rho(x+na) = \rho(x)$$

$$|\psi(x+na)|^2 = |\psi(x)|^2$$

The eigenfunctions is characterized by the Bloch vector k

$$\psi_k(x+na) = e^{ikna}\psi(x)$$

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

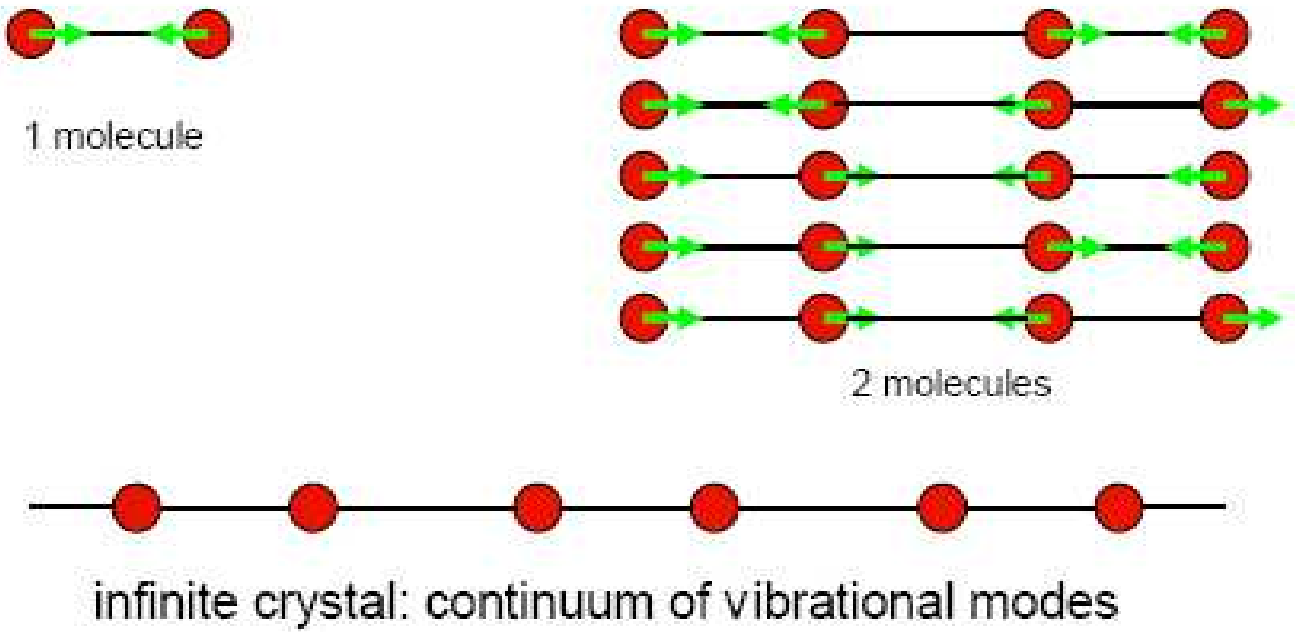
FIRST BRILLOUIN ZONE

CLASSICAL SIMULATION

INTERATOMIC POTENTIAL

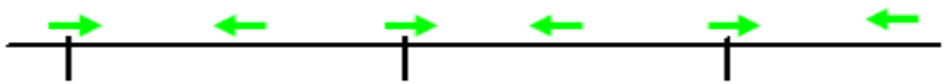
- coulombic interaction
- short term repusilve contribution
- Morse-like potential

VIBRATIONS

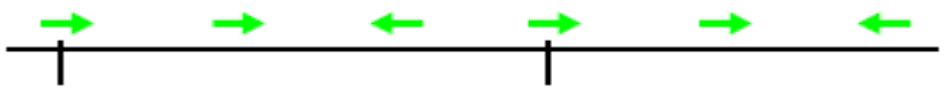

1 molecule
2 molecules
infinite crystal: continuum of vibrational modes

VIBRATIONS

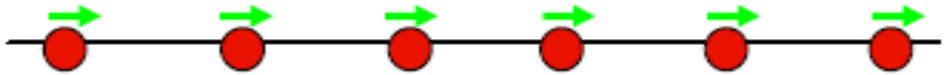
$\lambda = 2a, k = \pi/a$



$\lambda = 3a, k = 2\pi/3a$



$\lambda = \infty, k = 0$

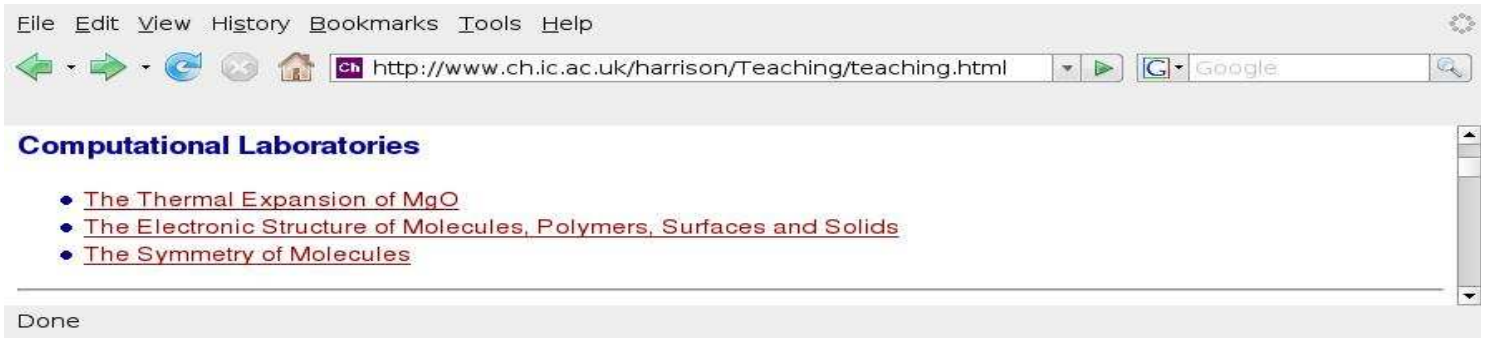


HELTZMON FREE ENERGY

$$F = E_0 + \frac{1}{2}\sum_{k,j} \hbar\omega_{j,k} + k_B T \sum_{k,j} \ln\left[1 - \exp(-\hbar\omega_{j,k} / k_B T)\right]$$

FIRST STEP

1. Restart the PCs that are running Windows;
2. Once you have a black screen with the following line:
   > **boot:**
   Type linux
   > **boot: linux**
   Press Enter
3. Use your login and passwd as in Window
4. Open firefox: the web browser
5. http://www.ch.ic.ac.uk/harrison/Teaching/teaching.html



HOW TO WRITE A REPORT I
by Giulia C. De Fusco

Introduction

- the system
- the methodology (theory in use)
- the aims of the exercise
- the tools in use (programs)

Body of the text

- write it like a scientific paper (well-articulated sentences, NOT a list of two-word answers)
- analyse *critically* obtained data and given answers
- round numerical answers to a specific number of decimal places (i.e. 4)
- add literature/web citations whenever a comparison with experimental data is required
- check spelling

HOW TO WRITE A REPORT II
by Giulia C. De Fusco

Pictures

- max 20
- reasonably sized (NOT one-page sized pictures, but still readable)
- described in caption or in the text

Graphs

- add labels and units
- add a *critical* comment whenever required (NOT a merely descriptive comment)

Conclusions

- give a general description of your calculations and your main findings

THANK YOU!!!